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THE EFFECT OF AlF_3 , B_2O_3 , AND KAOLINITE ADDITIVES ON THE RATE OF MULLITE FORMATION FROM OXIDES

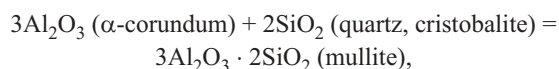
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Kinetic parameters of mullite formation from oxides in the presence of mineralizers (B_2O_3 and AlF_3) and with a kaolinite additive (20%) are experimentally studied. The degree of completion, the activation energy, and the velocity constants of the mullite-formation reaction in different mixtures are determined. It is demonstrated that AlF_3 and kaolinite have the most perceptible accelerating effect.

Mullite is a most important mineral materials for refractories and other ceramics. Studies of mullite-formation reactions, despite substantial research carried out in this field, still are not only of theoretical but also of practical interest.

The present study represents the results of experimental research of kinetic parameters of a reaction of mullite formation from oxides:



which proceeds in the presence of mineralizers B_2O_3 and AlF_3 and also with an initial kaolinite additive. It was earlier established [1] that the activation energy of this reaction taking place in a mixture of quartz and technical alumina without mineralizers and kaolinite additives is equal to 499.57 kJ/mole, and the reaction rate constant is a function of the temperature and amounts to

$$K = 3.1 \times 10^{12} \exp \left(-\frac{499,570}{RT} \right),$$

where R is the gas constant, J/mole.

The initial samples were tablets molded of a mixture of finely pulverized synthetic α -corundum and quartz powders (weight 1 g), whose chemical composition corresponds to mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Furthermore, the following additives were introduced into the mixture (here and elsewhere wt.%): 3 AlF_3 (mixture 3), 3 AlF_3 and 20 kaolinite (mixture 1), 3 B_2O_3 and 20 kaolinite (mixture 4). The size of initial quartz and corundum grains was 0.001–0.005 mm.

The samples were placed into a furnace with chromite-lanthanum heaters preheated to a required temperature and

held for a required time in air at temperatures of 1300, 1350, 1400, 1450, and 1500°C. The exposure duration varied from 0.5 to 5 h (spacing of 0.5 h) at 1400 and 1500°C and lasted 6 h at other temperatures.

After the experiments the samples were subjected to microscopic and x-ray analysis. It was found that the size of the crystals of newly formed mullite is very small and constitutes 0.002–0.007 mm, sometimes reaching 0.01–0.05 mm. The biggest number of mullite microcrystals is observed in mixtures containing initial kaolinite and mineralizer AlF_3 .

X-ray phase analysis demonstrated (Table 1) that the newly formed phases are mullite and cristobalite, whose quantities grow with increasing temperature and duration of the experiments. An x-ray-amorphous phase is formed in a very insignificant amount (and not always). The initial phases are corundum and quartz, whose content diminishes, and kaolinite, which disappears even in the shortest experiments. Based on the specifics of the x-ray patterns [2, 3], the synthesized mullite can be regarded as mullite of normal composition of 3 : 2 ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). As for the volatile components, i.e., AlF_3 , B_2O_3 , and H_2O (formed in decomposition of kaolinite), their incorporation in the mullite structure at such high temperatures as 1300–1500°C and extremely low degrees of volatilization appears virtually impossible. For example, a compound known as x-andalusite, which is hydroxyl-containing mullite, at a temperature of 1100°C loses its OH groups.

Thus, it follows from the experimental results that the reaction of mullite formation from oxides in different mixtures proceeds according to the above specified scheme. The role of mineralizers AlF_3 , B_2O_3 , and H_2O is presumably reduced to their known catalytic effect and, possibly, to the formation of an insignificant quantity of an intergranular melt due to a reaction with quartz, as can be seen in the SiO_2 – B_2O_3 system [4].

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TABLE 1

Temperature, °C	Duration of experiment, h	Initial mixture 3		Initial mixture 1		Initial mixture 4	
		$\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{AlF}_3$	degree of completion of reaction	kaolinite + $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{AlF}_3$	degree of completion of reaction	kaolinite + $\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{B}_2\text{O}_3$	degree of completion of reaction
1300	6.0	Quartz, cristobalite, corundum	0.04	Mullite, corundum, quartz (little), cristobalite	0.27	Cristobalite, quartz, corundum, mullite	0.11
1350	6.0	Cristobalite, quartz, corundum, mullite	0.04	Mullite, quartz, cristobalite, corundum	0.36	The same	0.16
1400	0.5	The same	0.06	The same	0.30	Quartz, corundum, mullite	0.16
1400	1.5	"	0.08	"	0.38	Cristobalite, quartz, corundum, mullite	0.19
1400	2.0	—	—	—	—	Quartz (traces), cristobalite (traces), corundum, mullite	0.20
1400	2.5	Cristobalite, quartz, corundum, mullite	0.09	Mullite, quartz, cristobalite, corundum	0.43	The same	0.22
1400	3.0	—	—	—	—	"	0.23
1400	3.5	Cristobalite, quartz, corundum, mullite	0.10	Mullite, quartz, cristobalite, corundum	0.46	—	—
1400	4.0	The same	0.10	—	—	Quartz (traces), cristobalite (traces), corundum, mullite	0.24
1400	4.5	—	—	Mullite, quartz, cristobalite, corundum	0.50	Quartz, corundum, mullite, cristobalite (traces)	0.24
1400	5.0	Cristobalite, quartz, corundum, mullite	0.11	—	—	—	—
1400	5.5	The same	0.12	Mullite, quartz, cristobalite, corundum	0.55	Cristobalite (traces), quartz (traces), corundum, mullite	0.28
1400	6.0	"	0.12	The same	0.58	The same	0.29
1450	6.0	"	0.23	"	0.60	Cristobalite, quartz (traces), corundum, mullite	0.44
1500	0.5	Cristobalite (little), quartz (little), corundum, mullite	0.32	—	—	—	—
1500	1.0	—	—	Mullite, corundum, quartz (traces)	0.76	—	—
1500	1.5	Cristobalite (little), quartz (little), corundum, mullite	0.37	The same	0.78	Quartz (traces), corundum, mullite	0.65
1500	2.0	—	—	—	—	The same	0.67
1500	3.0	Cristobalite (little), quartz (little), corundum, mullite	0.42	Mullite, corundum	0.84	—	—
1500	4.0	The same	0.45	—	—	—	—
1500	4.5	—	—	Mullite, corundum, amorphous phase	0.90	Quartz (traces), corundum, mullite	0.77
1500	5.0	Quartz (traces), corundum, mullite	0.48	—	—	The same	0.78
1500	5.5	Cristobalite (traces), corundum, mullite	0.50	Mullite, corundum, amorphous phase	0.94	"	0.80
1500	6.0	—	—	The same	0.96	"	0.82

Reactions between quartz and cristobalite are of special interest. At a temperature above 573°C , α -quartz is easily transformed (a coherent transformation) into β -quartz, which, according to the Fenner scheme, at 870°C should transform into β -tridimite, and the latter at 1470°C should transform into β -cristobalite. However, in "dry" conditions, in particular, under heating in air (i.e., under a very insignificant pressure of water vapor) tridimite is usually is formed, and starting at about 1000°C (especially at 1200 – 1300°C), cristobalite is metastably formed from quartz, chalcedony, and silicon [1, 5]. It follows from our experiments (Table 1)

that at 1300°C quartz (β -modification) partly transforms into cristobalite, and both silica phases exist until the end of the reaction even at a high temperature (1500°C) and a long exposure (up to 6 h). This result agrees with the known conclusion that Al_2O_3 impurity significantly (by about 300°C) retards the transformation of quartz into cristobalite [1]. The presence of an amorphous phase in the products of experiments agrees (along with the specified possibility of the formation of an intergranular melt) with the assumption of the possibility of emergence of an intermediate vitreous phase in the course of β -quartz \rightarrow cristobalite transformation [1].

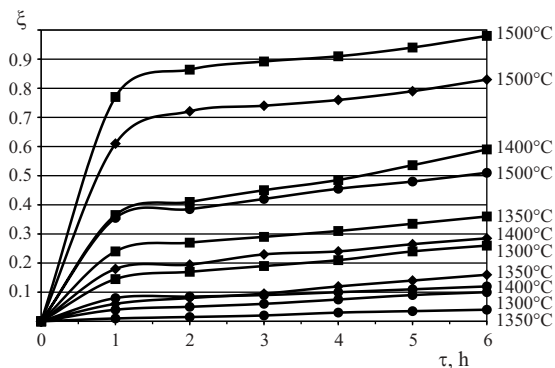


Fig. 1. Time dependence of the degree of transformation ξ in the reaction: $3\text{Al}_2\text{O}_3$ (α -corundum) + 2SiO_2 (quartz, cristobalite) = $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite): (●) mixture 3: $\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{AlF}_3$ (3%); (■) mixture 1: $\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{AlF}_3$ (3%) + kaolinite (20%); (◆) mixture 4: $\text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{B}_2\text{O}_3$ (3%) + kaolinite (20%).

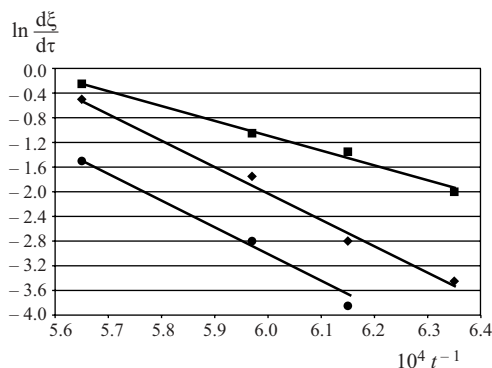


Fig. 2. Dependence of logarithms of velocities of the first stage of the reaction: $3\text{Al}_2\text{O}_3$ (α -corundum) + 2SiO_2 (quartz, cristobalite) = $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite). Same designations as in Fig. 1.

In order to obtain kinetic parameters of this reaction, quantitative x-ray analysis of samples was carried out. The percentage of the formed mullite with respect to 100% mullite yield, i.e., the degree of completion of the reaction, was calculated based on multiple determination of the intensities of mullite reflections (110) and (220) on the x-ray patterns after experiments. The results of the phase analysis and the quantitative x-ray study of the samples after experiments together with experimental parameters are indicated in Table 1. These results were used to plot dependences of the degree of transformation ξ on the process duration τ (Fig. 1). Kinetic data for kaolinite are not indicated in Fig. 1, since even in the shortest experiments (0.5 h) the reaction of mullite formation becomes virtually completed. It follows from Fig. 1 that:

- the reaction of mullite formation from oxides has the lowest rate in mixture 3 and the highest rate in mixture 1;
- the reaction of mullite formation from oxides can be arbitrarily divided into two stages: at the first stage lasting up to 1 h, the reaction is very fast (is 60–75% complete), especially at high temperatures, and the dependence of ξ on τ is

close to exponential; at the second stage lasting up to 5 h, the reaction proceeds slowly, the dependence of ξ on τ is close to a linear, and the reactions rates ($d\xi/d\tau$) of all mixtures differ insignificantly (lying within an interval of $0.01 - 0.03 \text{ h}^{-1}$).

The high reaction rate at the first stage is due to intense formation of mullite seeds. This is confirmed by the fact that the reaction is sharply accelerated when kaolinite is added to the initial mixture. Formation of mullite crystals (via a meta-kaolinite phase) on microareas of kaolinite occurs very quickly (in the first 10 min), starting with a temperature 950–1000°C [6]. This process is accompanied by release of water and formation of amorphous silica, which later is transformed into cristobalite [7]. Obviously, at the first stage, the fastest processes are the surface crystallization of mullite and intergranular and surface diffusion of the components (mainly SiO_2 [1]) due to a catalytic effect of the volatile mineralizers (Al_2O_3 and B_2O_3) and water vapor still persisting in a consolidated sample. A melt can be formed in a small quantity due to reactions between the volatile components and the SiO_2 phase. All this initiates intense formation of mullite from Al_2O_3 and SiO_2 .

The low reaction rate at the second stage is probably due to the fact that the controlling factor at this stage is relatively slow (due to a loss of Al_2O_3 , B_2O_3 , and H_2O) intergranular diffusion of the components, mainly SiO_2 [1]).

The shape of the kinetic curves of mullite-formation reactions (Fig. 1) resembles the kinetic curves of disintegration of kyanite, andalusite, and sillimanite into mullite + quartz [8]. The same author also notes the role of seed formation and the diffusion processes in the mullite-formation reaction.

The mean velocities of the reaction were determined for the fast first stage in an interval of 0–1 h. At temperatures of 1300 and 1350°C the velocities could be determined only approximately (for mixture 3 one could speak of a sufficiency high accuracy, and for mixture 4 at 1300°C the accuracy was lower). The logarithms of these velocities are indicated in Fig. 2.

On the basis of the angles of slope of curves in Fig. 2, the activation energy E and the pre-exponential multipliers of the velocity constant K were determined for the fast stage of the mullite-formation reactions in different mixtures:

– mixture 3:

$$E = 430.95 \text{ kJ/mole}, K = 1.72 \times 10^{12} \exp\left(-\frac{430,950}{RT}\right);$$

– mixture 1:

$$E = 188.28 \text{ kJ/mole}, K = 2.66 \times 10^5 \exp\left(-\frac{188,280}{RT}\right);$$

– mixture 4:

$$E = 294.13 \text{ kJ/mole}, K = 2.76 \times 10^8 \exp\left(-\frac{294,130}{RT}\right).$$

Research demonstrated that the energy of activation of the reaction of mullite formation from oxides [1] significantly decreases in the presence of B_2O_3 and AlF_3 mineralizers (especially, of the latter) and especially in the pre-

sence of kaolinite. This results agrees with the reaction rate at the first stage. It is worth noting that the values of activation energy and pre-exponential multiplier for mixture 3 are close to these values in the equation of the rate constant proposed by A. S. Berezhnoi and R. A. Kordyuk [1]. This corroborates the assumption that decomposition of added kaolinite has the most significant catalytic effect on the reaction of mullite formation from oxides.

Thus, kinetic curves of the reaction of mullite formation from oxides in the presence of mineralizers AlF_3 and B_2O_3 are obtained. AlF_3 and kaolinite added in a significant quantity (20%) have the most substantial catalytic effect. The role of kaolinite is presumably reduced to a very fast formation of mullite seeds and to a catalytic effect produced by released water vapor.

The above results are of technological interest, since they make it possible to identify optimum conditions for the production of mullite ceramics.

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